

# CARBON BLACK AND CARBON BLACK-CONDUCTING POLYMER COMPOSITES FOR ENVIRONMENTAL APPLICATIONS

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## INTRODUCTION

A large fraction of the carbon black commercially produced in the U. S. and other parts of the world goes into the automobile tire industry and other rubber applications. However, specialty applications of this material are expected to grow in the future. The present study explores the applicability of composites of carbon black and an electronically conductive polymer, polypyrrole, in environmental pollution abatement scenarios.

Chromium was used as a model environmental pollutant for demonstration of our approach. Chromium occurs in two common oxidation states in nature, Cr(III) and Cr(VI). Because it is only weakly sorbed onto inorganic surfaces, Cr(VI) is notoriously mobile in nature. On the other hand, Cr(III) is readily precipitated or sorbed on a variety of inorganic and organic surfaces at near neutral pH. The properties of Cr(III) and Cr(VI) have been reviewed with respect to acute and chronic toxicity, dermal toxicity, systemic toxicity, toxicokinetics, cytotoxicity, genotoxicity and carcinogenicity [1]. The hexavalent chromium compounds appear to be 10-100 times more toxic than their Cr(III) counterparts when both are administered by the oral route. The toxicology of chromium does not reside with the elemental form but varies greatly among a wide variety of many different chromium compounds. Oxidation state and solubility appear to be crucial factors in the regard [1]. Other aspects of chromium toxicity and carcinogenesis have been reviewed [2].

Reduction of Cr(VI) to Cr(III) followed by a pH adjustment to form the highly insoluble  $\text{Cr}(\text{OH})_3$  species would clearly be an effective means to counter the harmful effects of this element on the environment. It is worth noting that a wide variety of anthropogenic sources generate Cr(VI) in effluent streams: Chrome plating, electronic, metallurgical, timber, and leather tanning industries to name a few. Chemicals such as  $\text{SO}_2$ ,  $\text{FeSO}_4$  or sodium metabisulfite are currently used for Cr(VI) reduction. However, these chemicals are consumed in the process which also generates sludge and consequent solid waste handling problems.

We demonstrate herein a new electrochemical strategy for the environmental remediation of Cr(VI) that is based on *spontaneous* electron transfer to Cr(VI) from a pre-reduced conducting polymer (polypyrrole)-carbon black composite thus reducing Cr(VI) to the trivalent form. In doing so, the composite itself is oxidized, and can be *electrochemically recycled* back to the reduced state for a fresh treatment cycle. The present work builds upon an earlier effort [3] in these laboratories that utilized polypyrrole as the active material.

## EXPERIMENTAL

The carbon black-polypyrrole composites and the parent conducting polymer were chemically synthesized. Polypyrrole was chemically synthesized from an aqueous 0.1 M pyrrole solution using potassium persulfate as the oxidant. Further details of the preparation procedure and characterization are contained elsewhere [4].

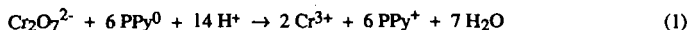
The polypyrrole-carbon black composite was prepared in a similar manner except that the polymerization medium contained in addition, the requisite amount of the N135 black [4]. Nominally, a composite containing ~43% (by wt.) of carbon black was utilized. In other experiments, the relative amount of polypyrrole and carbon black in the composite was varied by correspondingly varying the carbon black content of the polymerization medium [3]. For preparation of PVC-polypyrrole and PVC-carbon black composite, appropriate quantities of the two components were thoroughly mixed together (in a mortar and pestle) to afford ~43 wt.% of the active material (polypyrrole or carbon black). A similar procedure was also adopted in one instance for preparation of the polypyrrole-carbon black composite.

In all the experiments for this pilot study, pelletized rectangular-shaped samples were used. The pellet dimensions were chosen to fit inside a 1 cm path length quartz optical cuvette. The Cr(VI) solution comprised 1 mM of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 0.1 M  $\text{H}_2\text{SO}_4$  yielding an initial concentration of Cr(VI) of 104 ppm. In a typical experiment, 2 mL of this solution were pipetted into the cuvette. Chromium (VI) has an optical absorption band at 350 nm that can be used to monitor its concentration. The optical absorbance of the solution in contact with the pelletized active material, was monitored at requisite time intervals after initial contact. All tests were performed at the laboratory ambient temperature.

The efficacy of the polypyrrole-carbon black composite for Cr(VI) reduction was compared against three reference samples: polypyrrole, and composites of polypyrrole or carbon black with an *inert* matrix polymer, namely polyvinylchloride (PVC). The carbon black used in this study (N135) was made by a furnace process.

## RESULTS AND DISCUSSION

In a related study [3] we showed that spontaneous electron transfer occurs from an electrochemically pre-reduced polypyrrole sample to Cr(VI) consistent with a reaction scheme as follows:



In the above equation, PPy denotes polypyrrole and the superscripts "0" and "+" correspond to the reduced and oxidized states of the redox polymer respectively. Taking values for the standard reduction potential of  $-0.20\text{V}$  and  $+1.16\text{V}$  [3] respectively for the two redox couples in the above scheme, namely  $\text{PPy}^0/\text{PPy}^+$  and  $\text{Cr}^{6+}/\text{Cr}^{3+}$ , the process represented by Reaction 1 has a standard free energy change of  $-787 \text{ kJ/mol}$ . One potential advantage of this approach (over currently-used chemical treatment schemes) is that the active material, polypyrrole, can be repeatedly shuttled back and forth between its two redox states (Figure 1). On the other hand, for a heterogeneous process (such as ours), very high surface dispersion of the active material obviously is desirable, and carbon black can serve this function as a "surface modifier" component. Figure 2 contains data showing the ability of chemically synthesized polypyrrole to reduce Cr(VI). Half of the original Cr(VI) is reduced after  $\sim 35$  min. contact with polypyrrole as illustrated in Figure 2b. We presume (as verified by atomic absorption spectroscopy experiments in the previous case, Ref. 3) that most of the chromium resides in the solution phase as Cr(III). The solid line in Figure 2b is an exponential decay model fit to the data, consistent with first-order kinetics (see below).

Carbon black by itself can be compacted into a pellet; however it is much too fragile for routine handling and use in this form. Thus, PVC was chosen as an inert polymeric "binder." A pelletized sample of PVC alone gives no reduction of Cr(VI) during a 60 min. exposure. Next, a 40% (w/w) carbon black in PVC was prepared as described in the Experimental Section. The sample was first electrochemically pre-reduced (at  $-0.9 \text{ V}$ , all potentials herein quoted with respect to  $\text{Ag}/\text{AgCl}$  reference) in  $0.1 \text{ M H}_2\text{SO}_4$  prior to contact with the Cr(VI) solution; Figure 3 contains the results from this experiment. The lower Cr(VI) reduction rate in this case (relative to Figure 2) could be either a manifestation of the lower surface coverage of the active (carbon black) material, or an intrinsic difference between polypyrrole and carbon black. Nonetheless, the high activity of carbon black toward Cr(VI) was a bonus in terms of our new approach (see below). Again, the solid line in Figure 3b is an exponential decay model fit to the data.

Figure 4a contains data from an experiment wherein the potential of a carbon black-PVC composite electrode was continuously monitored during contact with Cr(VI). As before, the electrode was pre-reduced at  $-0.9 \text{ V}$ . On opening the circuit in  $0.1 \text{ M H}_2\text{SO}_4$ , the electrode potential gradually relaxes to the "rest" value. When the solution is subsequently dosed with Cr(VI), the potential undergoes a sharp excursion in the positive direction prior to attainment of a plateau. This excursion is symptomatic of the oxidation of the electrode surface by Cr(VI).

In order to examine whether the oxidation resulted in introducing oxygen functionalities at the carbon black surface, XPS spectra of the carbon black samples were compared before and after Cr(VI). No change in the C1s binding energy was noted. The lack of adsorption of chromium onto carbon black was also signaled by the absence of the chromium peaks at  $44 \text{ eV}$  ( $2 \text{ p}_1/2$ ),  $576 \text{ eV}$  ( $2 \text{ p}_{3/2}$ ) and  $586 \text{ eV}$  ( $2 \text{ p}_{1/2}$ ) in the XPS data. Similarly, experiments on samples before and after Cr(VI) contact show no significant change in  $L_c$  and  $L_a$  from the initial values of  $11.10 \text{ \AA}$  and  $23.50 \text{ \AA}$ , indicating that the material removal (by oxidation) occurs without alteration of the carbon black crystallite size within the matrix.

The driving force for electron transfer from carbon black to Cr(VI) can be tuned by controlling the potential of the former. This is shown in Figure 4b wherein three types of samples, namely a "neutral" (electrochemically untreated) specimen, a sample pre-oxidized at  $+0.9 \text{ V}$  and one pre-reduced at  $-0.9 \text{ V}$ , are compared in terms of their relative efficacy for Cr(VI) reduction. Electrochemical reduction raises the electron energy levels in the carbon black whilst the corresponding electronic states in the untreated and oxidized samples lie at lower energy levels. Stated in alternative terms, the reduction capacity of carbon black can be electrochemically tuned.

The PVC-carbon black composite exhibits classical electronic percolation behavior [21]. That is, there is a critical carbon black concentration in the matrix at which particle connectivity is established. Beyond this threshold (which occurs at  $\sim 20\%$  (w/w) of the black), rapid increase in the electronic conductivity occurs with further carbon black loading, quickly obtaining a plateau [4]. Figure 5 contains Cr(VI) conversion data for four different PVC-carbon black samples. Samples containing carbon black at levels below the percolation threshold exhibit negligible activity toward Cr(VI). Interestingly, there is an abrupt increase in the activity at the threshold beyond which only a modest increment occurs for the 40% (w/w) black PVC-carbon black sample.

Figure 6 contains a comparison of the relative efficacy of polypyrrole and carbon black for Cr(VI) reduction. These data were generated on three types of samples: a polypyrrole-carbon black composite, a reduced PVC-carbon black composite and a polypyrrole-PVC composite. The polypyrrole-carbon black composite contained  $\sim 43\%$  (w/w) of carbon black. To facilitate the

comparison, all these samples were "diluted" to the same extent with the PVC binder to afford 40% (w/w) of the active material. That is, the polypyrrole-carbon black composite in this particular experiment had a composition of 22.8% (w/w) polypyrrole, 17.2% (w/w) carbon black and 60% PVC in the final pelletized sample.

Interestingly, the composite containing *both* polypyrrole and carbon black as the active material exhibits the highest activity for Cr(VI) reduction. Further, carbon black (at least the grade used in this study) outperforms polypyrrole in its ability to reduce Cr(VI). The conversion data in Figure 7 can be fitted to a pseudo first-order kinetics scheme.

The influence of carbon black level in the polypyrrole-carbon black composite on the ability of the latter to reduce Cr(VI) was also considered. Contrary to the experiments considered earlier in Figure 6, the composite samples in this case were prepared *without* the PVC binder. A systematic improvement in the composite performance is noted with an increase in the carbon black content although the rate of improvement tends to saturate at the higher loadings.

## SUMMARY

This study has shown that the composites outperform both polypyrrole and carbon black in terms of their ability to reduce Cr(VI). It is worth noting that in the composite, both redox (polypyrrole) and oxidizable (carbon black) functions are built into the material framework. The former is reversible and the latter is irreversible. This is fortuitous in an economic sense in that carbon black is the less expensive of the two components, and can be periodically replenished. The stability of polypyrrole in repeat use cycles was also briefly explored in this study. No appreciable and systematic loss of conversion efficiency was noted over three Cr(VI) conversion cycles as long as the *electrochemical regeneration (reduction) step was essentially complete*. This latter process is a function of the polypyrrole morphology and the reduction potential used, and could encompass a time period anywhere from a few seconds to a few minutes. In our hands, a regeneration potential of  $-0.9$  V in  $0.1$  M  $H_2SO_4$  and a reduction time of 30 minutes were effective in restoring the activity of the sample.

We have used compacted samples for the active material in this study, merely for experimental convenience. A practical Cr(VI) treatment system can be envisioned to consist of a *packed bed* through which the effluent stream could be recirculated. This bed would comprise fine ( $\mu$ m size) particles of the polypyrrole-carbon black composite. Electrical contacts could be introduced via procedures routinely adopted for packed-bed electrochemical flow reactors (c.f. Ref. 5). Ideally, the charge-transfer kinetics at the active material/solution interface must be fast enough such that the system is under mass-transport control. Further efforts will focus on optimizing the Cr(VI) conversion kinetics at the polypyrrole-carbon black particle/solution interface. The fact that the reaction half-life is independent of the initial Cr(VI) concentration is encouraging in this regard.

A practical system would also require a pH adjustment step to immobilize the reduced Cr(III) onto the sample bed. The immobilized  $Cr(OH)_3$  could be reoxidized and released in a subsequent back-flushing cycle so that the Cr(VI) treatment system also regenerates Cr(VI) for fresh reuse. Further development of our Cr(VI) pollution abatement approach and the implementation of a practical system along the lines outlined in the previous paragraphs, are continuing in these laboratories.

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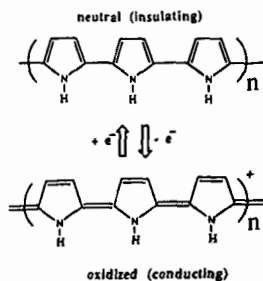


Figure 1. Neutral and oxidized redox states of polypyrrole and their inter-convertible nature.

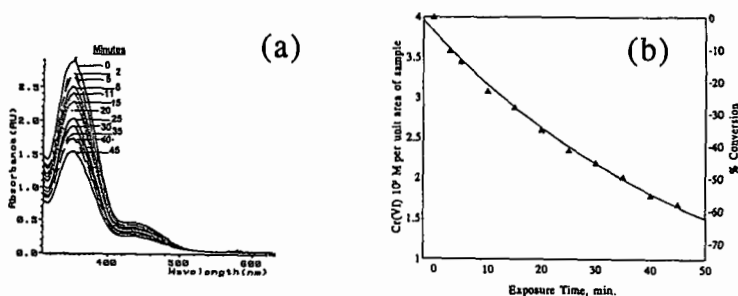


Figure 2.

Data illustrating the ability of chemically synthesized polypyrrole to reduce Cr(VI). UV-VIS spectra are shown in Figure 2a, and the Cr(VI) conversion vs. time computed from these spectral data are contained in Figure 2b. The numbers on the spectra in Figure 2a show the contact time with Cr(VI). The initial Cr(VI) solution composition is specified in the Experimental Section. The solid line in Figure 2b is a least-squares fit of the data (see text).

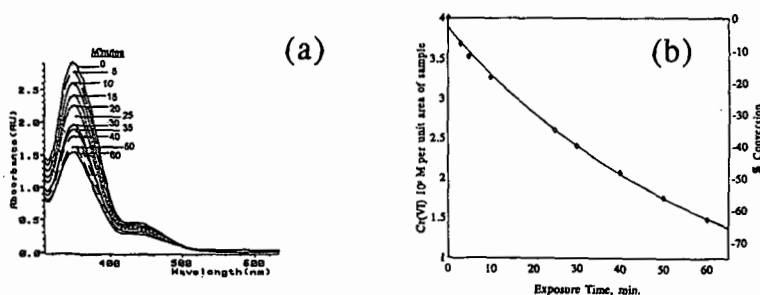


Figure 3.

Data illustrating the ability of carbon black to reduce Cr(VI). UV-VIS spectra are shown in Figure 3a, and the Cr(VI) conversion vs. time computed from these spectral data are contained in Figure 3b. The spectral notation in Figure 3a as in Figure 2a. The carbon black was dispersed in PVC to yield a composite containing 40% (w/w) of the black. The sample was first reduced at  $-0.9$  V in  $0.1$  M  $\text{H}_2\text{SO}_4$  prior to Cr(VI) contact.

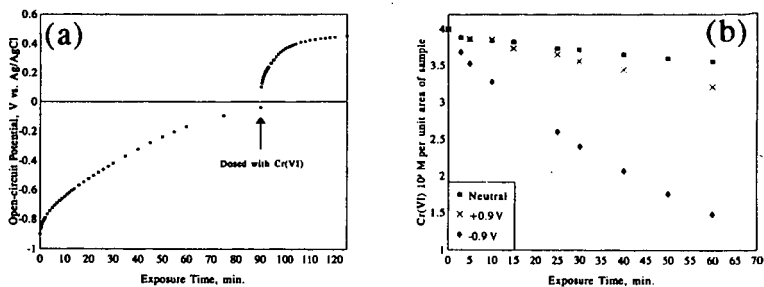


Figure 4. (a) Variation of the open-circuit potential of a PVC-carbon black composite electrode (30% w/w of carbon black) before and after contact with the Cr(VI) solution. The electrode was pre-reduced at -0.9V in 0.1 M H<sub>2</sub>SO<sub>4</sub> prior to opening the circuit and monitoring the potential. (b) Effect of electrochemical pre-treatment (in 0.1 M H<sub>2</sub>SO<sub>4</sub>) on the ability of a PVC-carbon black composite (30% w/w of carbon black) to reduce Cr(VI).

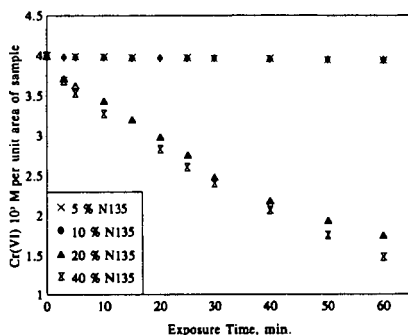


Figure 5. Influence of carbon black level (in the PVC-carbon black composite) on the Cr(VI) reduction ability of the composite. The percolation threshold in the composite occurs at ~20% (w/w) of the black (refer to text).

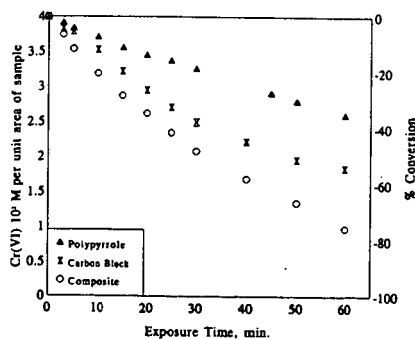


Figure 6. Comparison of the relative efficacy of polypyrrole, carbon black and the polypyrrole-carbon black composite for Cr(VI) remediation. The composite contained ~43% (w/w) of the black. In all the three cases, the active material was diluted to 40% by mixing with the inert PVC (refer to text).